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Effects of Li Doping on the Negative Bias Stress Stability of Solution-processed ZnO Thin Film Transistors

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To investigate the effect of Li dopant on the electrical characteristics under negative bias stress (NBS), we analysed ZnO and Li doped ZnO TFTs under NBS with -20 V for 10,800 s. The Li dopant enhanced the field effect mobility (8.21 cm²/V·s) and successfully sustained the variation of Vth of ZnO TFTs without any degradation of the field effect mobility.

The metal oxide semiconductors have been attracted as one of the most promising materials for the next generation displays including high resolution, transparent and flexible displays. The major benefits of metal oxides are the high electron mobility compared to amorphous silicon, the transparency in the visible spectrum, and the processibility of low-cost deposition methods at low-temperature compatible with polymer substrates. Although indium-gallium-zinc oxide (IGZO), one of the most studied compositions in metal oxide semiconductors, was applied to switching components of ultra-high definition displays, indium has the substantial drawback of scarcity.

Herein, to address the NBS stability issue, we investigate the effect of Li dopant on the electrical characteristics stability of solution-processed ZnO TFTs under NBS (Vth = -20 V) for 10,800 s. We respectively analysed the crystalline properties, the initial electrical characteristics, and the electrical characteristics stability after NBS of pristine ZnO and Li doped ZnO TFTs. In our comparative study, we found that Li dopant with the optimum concentration (10 mol%) does not distort the crystal structure of ZnO matrix, successfully enhances the initial field effect mobility and sustains the variation in Vth of ZnO TFTs without any degradation of the electrical characteristics after NBS.
To obtain reliable TFTs (figure 1a) with small variations of initial $V_{th}$, we investigated optimized concentration of the zinc ammine complex solution and various conditions of the spin-coating atmosphere. According to our previous reports, the concentration of the zinc ammine complex solution was increased up to 90 mM. We fabricated the ZnO film by spin-coating in a glove box using 83 mM and 90 mM of zinc ammine complex solution. The device from 83 mM and 90 mM zinc ammine complex solution exhibited the threshold voltage ($V_{th}$) of the device from 83 mM and 90 mM zinc ammine complex solution were obtained from ZnO powder, the intensity of (002) peak was substantial peak by grazing incidence XRD due to its thin thickness (about 5 nm). Figure 2b and d showed the XRD patterns of pristine ZnO and Li doped ZnO thin films. The nano-crystalline domains are clearly shown and the size of grains is less 10 nm. The lattice spacing of 0.262 nm and 0.261 nm was deduced from pristine ZnO and Li doped ZnO film, respectively. According to the lattice spacing of 0.260 nm for (002) ZnO crystal plane, we could speculate that our ZnO and Li doped ZnO films were oriented with the c-axis. However, as shown in figure S2 (see the ESI), 20 mol% (over optimized doping concentration) of Li dopant clearly distorted crystalline structure of ZnO with c-axis orientation. As lattice spacing of 0.281 nm and 0.248 nm correspond to (100) and (101) ZnO crystal plane, 20 mol % of the Li doped ZnO film is randomly disordered with (100) and (101) planes of ZnO. The XRD analyses were performed with the ZnO and Li (10 mol%) doped ZnO powder because our ZnO film on the Si wafer could not be detected any substantial peak by grazing incidence XRD due to its thin thickness (about 5 nm). Figure 2b and d showed the XRD patterns of pristine ZnO powder and Li doped ZnO powder from the zinc ammine complex solution with 60 V of drain voltage ($V_D$) and tested TFTs using 83 mM zinc ammine complex solution under the process condition of device D for stable operation-ability. Also, we used $V_{th}$ instead of $V_{th}$ because $V_{th}$ values have inconsistency depending on defining the saturation region.

In order to investigate the effect of Li doping on the crystalline properties of ZnO thin film, high resolution transmission electron microscopy (HR-TEM) and X-ray diffraction (XRD) analyses were performed. Figure 2a and c showed the top view image of HR-TEM of pristine ZnO and Li (10 mol%) doped ZnO thin films. The nano-crystalline domains are clearly shown and the size of grains is less 10 nm. The lattice spacing of 0.262 nm and 0.261 nm was deduced from pristine ZnO and Li doped ZnO film, respectively. According to the lattice spacing of 0.260 nm for (002) ZnO crystal plane, we could speculate that our ZnO and Li doped ZnO films were oriented with the c-axis. However, as shown in figure S2 (see the ESI), 20 mol% (over optimized doping concentration) of Li dopant clearly distorted crystalline structure of ZnO with c-axis orientation. As lattice spacing of 0.281 nm and 0.248 nm correspond to (100) and (101) ZnO crystal plane, 20 mol % of the Li doped ZnO film is randomly disordered with (100) and (101) planes of ZnO. The XRD analyses were performed with the ZnO and Li (10 mol%) doped ZnO powder because our ZnO film on the Si wafer could not be detected any substantial peak by grazing incidence XRD due to its thin thickness (about 5 nm). Figure 2b and d showed the XRD patterns of pristine ZnO powder and Li doped ZnO powder from the zinc ammine complex solution. The diffraction patterns exhibited three distinct peaks at 2 theta = 31.9°, 34.5°, and 36.6° indicating (100), (002), and (101) hexagonal ZnO crystal planes, respectively. Since XRD patterns were obtained from ZnO powder, the intensity of (002) peak was weak compared to other crystal plane peaks. If XRD patterns had been obtained with ZnO thin films deposited on Si wafer, we could expect the strong (002) peak the same as previously report. In accordance to the TEM results, we suggest that the Li dopant with optimum doping concentration (10 mol%) did not distort the crystallization of ZnO.

To investigate the effect of Li dopant on the stability of electrical characteristics ($V_{on}$, $V_{th}$, $\mu_F$, and S.S.) under NBS test, we fabricated and tested TFTs using 83 mM zinc ammine complex solution under the process condition of device D for stable operation-ability. Also, we used $V_{th}$ instead of $V_{th}$ because $V_{th}$ values have inconsistency depending on defining the saturation region.

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was biased on the gate electrode of pristine ZnO and Li (10 mol%) doped ZnO TFTs for 10,800 s. The measurement was performed under vacuum for eliminating the effect of instability by field-induced adsorption and desorption of oxygen molecules and water molecules.\(^{18}\) Figure 3a showed the electrical characteristics of pristine ZnO and Li doped ZnO TFTs, which consist of the average of \(V_{on}\), \(V_{th}\), the field effect mobility \(\mu_{FE}\) and the subthreshold slope (S.S.) of the initial state and the average of delta value after NBS. As expected, Li dopant increased the field effect mobility of Li doped ZnO TFTs compared to that of pristine ZnO TFTs. The maximum field effect mobility of Li doped ZnO TFT in the initial state was 8.21 cm\(^2\)/V∙s. In terms of the average subthreshold slope in the initial state, pristine ZnO and Li doped ZnO TFTs exhibited 1.98 and 2.12 V/decade, respectively. With these results, Li dopants increased the field effect mobility without any significant effects on the subthreshold slope in the initial state. After NBS, the subthreshold slope and the field effect mobility of both devices were improved. The average of the delta subthreshold slope of pristine ZnO and Li doped ZnO TFTs was -0.72 and -0.85 V/decade after NBS, respectively. Although the average of the delta field effect mobility of Li doped ZnO TFTs after NBS was -0.31 cm\(^2\)/V∙s by one deteriorated device (Li doped ZnO TFT sample #1 in figure 4f), except the deteriorated sample #1 of Li doped ZnO TFT, all Li doped ZnO TFTs showed the increase of field effect mobility (figure 4f). We assume the uncontrolled humidity condition of annealing process could affect the one deteriorated device. As similar as the changes of the field effect mobility of Li doped ZnO TFTs, the average delta field effect mobility of pristine ZnO TFTs after NBS also slightly increased (0.17 cm\(^2\)/V∙s). The average of shifted \(V_{on}\) of pristine ZnO and Li doped ZnO TFTs was -3.3 V and -3.84 V and the average of shifted \(V_{th}\) was -2.48 V and -4.65 V, respectively. Although the difference of the average shifted \(V_{on}\) between pristine ZnO and Li doped ZnO TFTs was -2.17 V, but the difference of the average shifted \(V_{on}\) was only -0.54 V. In the other words, the pristine ZnO and Li doped ZnO TFTs have a similar tendency for the \(V_{on}\) shift under NBS. When the field effect mobility of Li doped ZnO TFTs is much higher than that of pristine ZnO TFTs, there wasn’t any considerable difference in the \(V_{on}\) shift under NBS. Figure 3b-e showed the variation induced by NBS in \(V_{on}\), \(V_{th}\), the field effect mobility, and the subthreshold slope of both ZnO and Li doped ZnO TFTs in the form of the box chart, respectively. As shown in figure 3b-e, Li dopant with the optimum concentration (10 mol%) did not effect on the electrical characteristics of ZnO TFTs after NBS.

Figure 4a and d showed that the evolution of the transfer curves of pristine ZnO and Li doped ZnO TFTs, as a function of NBS time. The transfer curves showed a parallel shift of \(V_{on}\) in the negative direction without any significant changes of its shape. The output curves and hysteresis of the both devices after NBS were shown in figure S3 (see the ESI). The instability of metal oxide TFTs under bias stress could be elucidated by representative mechanisms: charge injection, charge trapping, state creation or ambient effect.\(^{18-21}\) These mechanisms have different effect on the variation of \(V_{th}\). The
charge injection model has a linear increase rate of $\Delta V_{on}$ versus logarithmic stress time and charge trapping has an exponential increase rate versus logarithmic stress time.\textsuperscript{22} The state creation mechanism causes a large $V_{on}$ shift by 10 V in case of the PLD deposited IGZO TFTs.\textsuperscript{21} Also, the instability mechanism from the ambient effect on the non-passivation device is excluded owing to the measurement was performed in the vacuum chamber as mention above. Figure 4b and e showed the exponential increase of $\Delta V_{on}$ of ZnO and Li doped ZnO TFT versus logarithmic stress time and we speculated that the instability of our devices caused by charge trapping mechanism. The changes of the field effect mobility of both devices versus stress time were shown in figure 4c and f. The variations of the field effect mobility and the $V_{th}$ of Li doped ZnO TFTs over stress time were similar to the results of ZnO TFTs. With these results, we assumed that Li dopant with optimized doping concentration with 10 mol% did not notably effect on the stability of electrical characteristics of ZnO TFTs under NBS, and it also had kept its higher field effect mobility. Therefore, the Li dopant could improve the field effect mobility without any changes of the variation in $V_{on}$ of ZnO TFTs after NBS.

The slight shift of $V_{on}$ of both devices in a negative direction is caused by trapping of accumulated positive charged ion (zinc interstitial (Zn) or oxygen vacancies from non-stoichiometric properties of ZnO) at the interface between semiconductor and dielectric layer.\textsuperscript{23} The accumulation of positive charged ion is derived from the applied negative bias stress on the gate electrode of both devices. The Li dopant which plays a role of electron donor did not significantly affect the non-stoichiometric properties of ZnO because Li dopant with the optimum concentration prefers interstitial sites over substitution sites in the ZnO matrix. As the difference of the migration energy between Zn$_i$ and Li$_i$ is as small as 0.04 ~ 0.11 eV, we speculate that the effect of Zn$_i$ and Li$_i$ on the variation in $V_{on}$ are quite similar.\textsuperscript{24,25} Therefore, there could be no significant difference of $V_{on}$ instability between pristine ZnO and Li doped ZnO TFTs.\textsuperscript{10} Besides, the increase of the field effect mobility of both devices after NBS could be explained by additional carriers. The additional carriers are from positively charged donor state above the Fermi level due to band bending when the negative bias is applied.\textsuperscript{23} The illustration of the band bending diagram is shown in figure S4 (see the ESI). Although other metal dopants such as Al, Y and Hf improved bias stress stability through suppressing the formation of oxygen vacancy, the field effect mobility was decreased due to reduction of carrier concentration.\textsuperscript{26–28} However, Li dopant with optimized concentration drastically increased the field effect mobility of ZnO TFT and retained a little shift of $V_{on}$ compared with that of pristine ZnO TFT after prolonged NBS. With these benefits of Li dopant which induces the high field effect mobility and negligible difference of $V_{on}$ shift compared to pristine ZnO TFs, Li could be a favourable dopant. If the bias stress stability of $V_{on}$ of solution-processed metal oxide (such as ZnO) TFs have been improved by passivation technology,\textsuperscript{29} Li will be useful dopant for realizing low-cost fabricated high resolution LCD displays.

Conclusions

To investigate the effect of Li dopant on the electrical characteristics under NBS, we fabricated the solution processed pristine ZnO TFs and Li (10 mol%) doped ZnO TFTs, then a constant -20 V was biased on the gate electrode of TFTs during 10,800 s. We deduced that Li dopant did not significantly influence on the electrical characteristics during NBS. The Li dopant enhanced the initial field effect mobility of pristine ZnO TFTs from 4.35 to 7.28 cm$^2$/V-s and did not aggravate the variation of the $V_{on}$ of pristine ZnO TFTs under NBS without the degradation of other electrical characteristics. For practical HD LCD applications of metal oxide TFTs, the high field effect mobility and the low variation in $V_{on}$ are a key factor, because the high field effect mobility alleviates a charging time issue for the capacitors in each scan line and the low variation of $V_{on}$ prevents the non-uniform brightness problems induced by substantial variation of $V_{on}$. Combined with various techniques which improve the $V_{on}$ stability of solution-processed metal oxide TFTs, the Li dopant could be an attractive dopant for a low-cost fabricated HD LCD because lithium effectively enhances the field effect mobility without degradation of $V_{on}$ stability under NBS.

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Notes and references